# THERMAL BARRIER COATING WITH MODULATED GRAIN STRUCTURE AND METHOD THEREFOR

#### **DESCRIPTION**

#### [Para 1] BACKGROUND OF THE INVENTION

[0001] The present invention generally relates to coatings for components exposed to high temperatures, such as the hostile thermal environment of a gas turbine engine. More particularly, this invention is directed to thermal barrier coatings having modulated columnar microstructures that increase the impact resistance of the coatings.

[Para 2] Components within the hot gas path of gas turbine [0002] engines are often protected by a thermal barrier coating (TBC). TBC's are typically formed of ceramic materials deposited by plasma spraying, flame spraying and physical vapor deposition (PVD) techniques. Various ceramic materials have been proposed for TBC's, the most widely used being zirconia (ZrO<sub>2</sub>) partially or fully stabilized by yttria (Y<sub>2</sub>O<sub>3</sub>), magnesia (MgO), or ceria (CeO<sub>2</sub>) to yield a tetragonal microstructure that resists phase changes. Yttriastabilized zirconia (YSZ), and particularly YSZ containing about six to eight weight percent yttria (6-8%YSZ), has been the most widely used TBC material due at least in part to its high temperature capability, low thermal conductivity, and relative ease of deposition by plasma spraying, flame spraying and PVD techniques. To promote adhesion of TBC to metallic substrates, such as superalloys used in gas turbine engine applications, a metallic bond coat is usually deposited on the substrate before applying the TBC. Bond coats are typically an aluminum-rich composition, such as an overlay coating of an MCrAIX alloy or a diffusion coating such as a diffusion aluminide or a diffusion platinum aluminide. As a result of oxidation, bond coats formed of these

compositions develop an aluminum oxide (alumina) scale that chemically bonds the TBC to the bond coat and the underlying substrate.

[Para 3] [0003] Spraying techniques deposit TBC material in the form of molten "splats," resulting in a TBC characterized by a degree of inhomogeneity and porosity. TBC's employed in the highest temperature regions of gas turbine engines are most often deposited by PVD, particularly electron-beam PVD (EBPVD), which yields a strain-tolerant columnar grain structure that is able to expand and contract without causing damaging stresses that lead to spallation. Similar columnar microstructures can be produced using other atomic and molecular vapor processes, such as sputtering (e.g., high and low pressure, standard or collimated plume), ion plasma deposition, and all forms of melting and evaporation deposition processes (e.g., laser melting, etc.).

[Para 4] [0004] In addition to being well adhered and having low thermal conductivities, TBC's on gas turbine engine components are required to withstand damage from impact by hard particles of varying sizes that are generated upstream in the engine or enter the high velocity gas stream through the air intake of a gas turbine engine. The result of impingement can be erosive wear (generally from smaller particles) or impact spallation from larger particles. Impact spallation is a primary issue at and near the leading edge of gas turbine engine blades and vanes, where the likelihood of damage from impact spallation is sufficiently high that the thermal protection of TBC deposited on a leading edge of a blade or vane is often not taken into consideration when designing the blade or vane. As a consequence, greater amounts of cooling air are necessary to maintain an acceptable blade/vane surface temperature.

[Para 5] [0005] Figure 1 depicts one of the mechanisms of damage caused by a particle 20 impacting a TBC 14 adhered with a bond coat 12 to a substrate 10. The TBC 14 is represented as having a columnar grain structure

of the type described above. As such, the TBC 14 comprises individual columns 16 separated by gaps 18, resulting in a porous microstructure. An interface 26 exists between the TBC 14 and bond coat 12, where adhesion between the TBC 14 and bond coat 12 is promoted by alumina scale (not shown). The impacting particle 20 generates stress waves 22 in the outer surface region of the impacted columns 16. The stress waves 22 travel downward through the impacted columns 16, arriving at the interface 26 as reflected stress waves 24. The stresses generated by the stress waves 22 and 24 are compressive in the first few columns 16, but become tensile in succeeding columns 16 (as viewed in Figure 1, those columns 16 to the right of the impacted columns 16). When these tensile stresses reach the interface 26 between the TBC 14 and bond coat 12, separation of the TBC 14 at the interface 26 can occur depending on the magnitude of the tensile stresses. In such an event, the TBC 14 completely separates (spalls) from the bond coat 12.

[Para 6] [0006] Commonly-assigned U.S. Patent No. 6,352,788 to Bruce teaches that YSZ containing about one up to less than six weight percent yttria in combination with magnesia and/or hafnia exhibits improved impact resistance. In addition, commonly-assigned U.S. Patent Application Serial No. 10/063,962 to Bruce shows that small additions of lanthana, neodymia and/or tantala to zirconia partially stabilized by about four weight percent yttria (4%YSZ) can improve the impact resistance of 4%YSZ. It would be desirable if further improvements in impact resistance could be obtained.

# [Para 7] BRIEF SUMMARY OF THE INVENTION

[0007] The present invention provides TBC's and methods of depositing TBC's having modulated columnar microstructures that increase the impact resistance of the coatings.

[Para 8] [0008] A TBC of this invention is formed of a ceramic material and has a columnar microstructure in which columns extend from the surface

of the substrate on which the TBC was deposited. The columns have inner regions contacting the substrate surface, outer regions near an outermost surface of the TBC, and interior regions therebetween. The inner regions of the columns are substantially normal to the surface of the substrate, while at least one of the interior and outer regions of the columns are nonaligned with their inner regions, so that the columns of the columnar microstructure are continuous but modulated between the inner and outer regions to reduce tensile stresses within the columns resulting from particle impact. According to the invention, such modulation of the columns reduces the likelihood that cracks resulting from particle impact will form in the inner regions of the columns, and instead will more likely form within the outer regions of the columns, with the result that impact damage of the TBC is similar to erosive wear instead of impact spallation.

[Para 9] [0009] TBC's as described above can be deposited by a line-of-sight vapor deposition technique that involves continuous or reversing rotation of the substrate about an axis of rotation thereof, and also oscillation (pitching) of the axis of rotation. During deposition of the inner regions of the columns, the axis of rotation of the substrate is oriented substantially perpendicular to the direction of vapor flow from a source of the ceramic material. To deposit the interior and outer regions of the columns, the axis of rotation is oscillated (pitched) relative to the vapor flow direction.

[Para 10] [0010] A significant advantage of this invention is the improved impact resistance associated with the modulated columnar structure of the TBC above the inner regions of the TBC columns. As a result of the modulated columnar structure, TBC separation/spallation can be inhibited to the extent that spallation at the leading edge of a turbine blade or vane is significantly reduced or eliminated, thereby reducing the amount of cooling air required by the blade/vane. Another advantage is that existing processing technology can be readily operated to achieve the desired microstructures and performance.

[Para 11] [0011] Other objects and advantages of this invention will be better appreciated from the following detailed description.

### [Para 12] BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 represents a fragmentary cross-sectional view of an impact event occurring in a columnar TBC.

[Para 13] [0013] Figures 2 and 3 schematically represent fragmentary cross-sectional views of TBC's having modulated columnar grain structures in accordance with two embodiments of this invention.

[Para 14] [0014] Figure 4 is a scanned image of a cross-section of a prior art TBC that suffered localized spallation as a result of impact damage.

[Para 15] [0015] Figures 5 and 6 are scanned images of cross-sections of TBC's with modulated columnar grain structures in accordance with the present invention.

[Para 16] [0016] Figure 7 schematically represents a portion of a line-of-sight deposition apparatus for carrying of processes capable of depositing modulated columnar TBC's of this invention.

# [Para 17] DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention is applicable to a variety of components subjected to high temperatures, such as the high and low pressure turbine nozzles and blades, vanes, shrouds, combustor liners and augmentor hardware of gas turbine engines. The invention is particularly desirable for use on high pressure turbine blades and vanes, whose leading edges are subjected to particulate impact. The TBC is part of a TBC system that typically

includes a metallic bond coat that bonds the TBC to the component surface. The bond coat is preferably an aluminum-rich diffusion coating, an MCrAIX overlay coating, or a more recently developed beta-phase NiAI intermetallic overlay coating of a type disclosed in commonly-assigned U.S. Patent Nos. 5,975,852 to Nagaraj et al., 6,291,084 to Darolia et al., 6,153,313 to Rigney et al, and 6,255,001 to Darolia. Such a bond coat develops an aluminum oxide (alumina) scale as a result of oxidation during deposition of the TBC and high temperature excursions during engine operation. The alumina scale chemically bonds the TBC to the bond coat and, therefore, the underlying component surface.

[Para 18] [0018] The TBC can be formed of a variety of ceramic materials, a notable example of which is zirconia partially stabilized by yttria (e.g., about 4-8 wt.% YSZ). Other suitable ceramic materials for the TBC include materials formulated to have lower coefficients of thermal conductivity (low-k) than 7%YSZ, notable examples of which are disclosed in commonly-assigned U.S. Patent No. 6,586,115 to Rigney et al., U.S. Patent No. 6,686,060 to Bruce et al., commonly-assigned U.S. Patent Application Serial Nos. 10/063,962 to Bruce, 10/064,785 to Darolia et al., and 10/064,939 to Bruce et al., and U.S. Patent No. 6,025,078 to Rickerby. Still other suitable ceramic materials for the TBC include those that resist spallation from contamination by compounds such as CMAS (a relatively low-melting eutectic of calcia, magnesia, alumina and silica). For example, the TBC can be formed of a material capable of interacting with molten CMAS to form a compound with a melting temperature that is significantly higher than CMAS, so that the reaction product of CMAS and the material does not melt and infiltrate the TBC. Examples of CMASresistant coatings include alumina, alumina-containing YSZ, and hafnia-based ceramics disclosed in commonly-assigned U.S. Patent Nos. 5,660,885, 5,683,825, 5,871,820, 5,914,189, and 6,627,323 and commonly-assigned U.S. Patent Application Serial Nos. 10/064,939 and 10/073,564, whose disclosures regarding CMAS-resistant coating materials are incorporated herein by reference. Other potential ceramic materials for the TBC include those formulated to have erosion and/or impact resistance better than 7%YSZ.

Examples of such materials include certain of the above-noted CMAS-resistant materials, particularly alumina as reported in U.S. Patent No. 5,683,825 and U.S. Patent Application Serial No. 10/073,564. Other erosion and impact-resistant compositions include reduced-porosity YSZ as disclosed in commonly-assigned U.S. Patent Application Serial Nos. 10/707,197 and 10/708,020, fully stabilized zirconia (e.g., more than 17%YSZ) as disclosed in commonly-assigned U.S. Patent Application Serial No. 10/708,020, and chemically-modified zirconia-based ceramics. Finally, TBC's of particular interest to the present invention have a strain-tolerant microstructure of columnar grains. As known in the art, such columnar microstructures can be achieved by depositing the TBC using a physical vapor deposition technique, such as EBPVD or another atomic and molecular vapor process, as well as known melting and evaporation deposition processes. The TBC is deposited to a thickness that is sufficient to provide the required thermal protection for the component, generally on the order of about 75 to about 300 micrometers.

[Para 19] [0019] Figures 2 and 3 represent two of multiple possible TBC microstructures within the scope of the present invention. In each case, a TBC 32 and 42 is shown deposited on a substrate 30, which may be the surface of a component or a coating on a component, such as the superalloy 10 and bond coat 12, respectively, of Figure 1. In addition, each TBC 32 and 42 is shown as having a columnar microstructure comprising discrete, continuous columns 34 and 44 that extend from the surface of the substrate 30 to the outermost surface of the TBC 32 and 42. As such, the TBC's 32 and 42 do not contain discrete layers of columns separated by distinct interfaces. As typical with columnar TBC microstructures, the columns 34 and 44 are generally equally spaced from each other along their lengths.

[Para 20] [0020] In Figure 2, the TBC 32 generally has three regions: an inner region 36, an outermost surface region 38, and an interior region 40 therebetween. The inner region 36 of each column 34 can be seen to be oriented substantially perpendicular to the surface of the substrate 30. The

surface regions 38 of the columns 34 are not aligned with their respective inner regions 36, which as used herein means the axes of the columns 34 within their inner and surface regions 36 and 38 are not coaxial or parallel. Furthermore, the columns 34 within the interior region 40 are not linear, but instead the axes of the columns 34 follow substantially parallel paths that are periodically diverted in one direction and then another (e.g., opposite) direction. The TBC 42 represented in Figure 3 is also indicated as generally having an inner region 46, an outermost surface region 48, and an interior region 50. As with the TBC 32 of Figure 2, the inner region 46 of each column 44 is substantially perpendicular to the surface of the substrate 30, and thereafter the axes of the columns 44 follow substantially parallel paths that are periodically diverted in one direction and then another (e.g., opposite) direction. In contrast to Figure 2, the axes of the columns 44 within the surface and interior regions 48 and 50 are substantially coaxial or at least parallel (and therefore aligned) with their respective inner regions 46, except for localized regions 52 within the interior region 50 in which excursions of the columns 44 periodically and briefly occur. In each of Figures 2 and 3, the organized, coherent and coinciding changes in directions of the column axes along the lengths of the columns 34 and 44 create what is termed herein a modulated microstructure.

[Para 21] [0021] According to the invention, the substantially perpendicular orientation of the inner regions 36 and 46 of the columns 34 and 44 promotes adhesion of the TBC's 32 and 42 to the substrate 30, while the modulations created in the columnar microstructures of the TBC's 32 and 42 above their inner regions 36 and 46 reduce the magnitude of the tensile stresses that reach the inner regions 36 and 46 of the columns 34 and 44 and the interface between the TBC's 32 and 42 and their underlying substrates 30. As a result, instead of TBC separation at the interface with the substrates 30, the TBC columns 34 and 44 are more likely to crack within the outer surface regions 38 and 48 of the TBC's 32 and 42. In this manner, particle impact damage to the TBC's 32 and 42 is more likely to occur in the form of eroding

and/or chipping away of the columns 34 and 44 as the stress waves travel downward through the columns 34 and 44, such that the damage due to impact events is essentially converted from impact spallation to a gradual removal of the TBC's 32 and 42 by surface erosion and chipping.

[Para 22] [0022] While the inner, interior and outer regions 36, 38, 40, 46, 48, and 50 may be deposited to have the same composition, it is foreseeable that they could be formed of different materials to enhance the overall properties of the TBC's 32 and 42. For example, the inner regions 36 and 46 could be formed of a conventional YSZ composition (e.g., 7%YSZ), while one or both of the interior and outer regions 38, 40, 48, and 50 could be formed of one or more of the above–noted materials having lower thermal conductivities, greater CMAS–resistance, and/or greater erosion resistance than the underlying YSZ of the inner regions 36 and 46.

[Para 23] [0023] Modulated TBC microstructures of the type represented in Figures 2 and 3 can be obtained by combinations of rotation, rocking, and oscillation motions performed with the surface being coated (e.g., the substrates 30 of Figures 2 and 3) during the process of depositing the TBC's 32 and 42. Rotation is meant to refer to the rotation of a component about an axis thereof, while a rocking motion is the periodic reversal of a rotational movement. As used herein, oscillation refers to the periodic pitching of the rotational axis of a component. For example, with a component oriented so that its axis of rotation is generally perpendicular to a line between the component and the source of the coating material being deposited, oscillation may be performed between the initial, generally horizontal orientation of the component to a pitch-up or pitch-down orientation relative to the source.

[Para 24] [0024] While a variety of combinations of rotation/rocking and oscillation are possible, the following sets forth six particular examples of deposition processes believed to be capable of producing modulated TBC

microstructures of the type described above. The processes presume deposition is carried out by a line-of-sight process such as EBPVD, though it should be understood that another atomic and molecular vapor process, as well as other known melting and evaporation deposition processes, could be used. As discussed above and represented in Figure 7, all of these processes are carried out so that the component (e.g., blade or vane) 60 is initially horizontally oriented directly above a source (e.g., ingot) 62 of the coating material, so that the axis of rotation 64 of the component 60 is generally perpendicular to an imaginary line 66 between the component 60 and the source 62. As used herein, the terms "oscillate" and "pitch" refer to a change in the orientation of the component 60 that results in a change in the angle between the component axis 64 and the imaginary line 66. Finally, values for such process parameters as rotational speed, oscillation angles, time periods, are provided, though such values are to be considered only suitable examples. For example, rotational speeds of about 2 to 20 rpm are believed to be acceptable for carrying out the invention. Furthermore, coating processes are generally targeted for completion in about 600 to about 3000 seconds, though longer and shorter processes are also within the scope of the invention.

# [Para 25] [0025] Constant rotation with on/off oscillation:

- a. Initiate coating process by depositing for about 120 seconds while the component is substantially horizontal and is rotated at a substantially constant 14 rpm.
- b. For a period of about 400 seconds, deposit while the component is oscillated between horizontal and a forty-degree down orientation and while maintaining 14 rpm constant rotation.
- c. Discontinue oscillation and, with the component again oriented horizontally, maintain 14 rpm constant rotation for about 150 seconds.
- d. Repeat step b.
- e. Repeat step c.
- f. Repeat step b.

# [Para 26] [0026] Rocking rotation with on/off oscillation:

- a. Initiate coating process by depositing for about 120 seconds while the component is substantially horizontal and is rotated at a substantially constant 14 rpm.
- b. For a period of about 400 seconds, deposit while the component is oscillated between horizontal and a forty-degree down orientation and while maintaining 14 rpm constant rotation.
- c. Discontinue oscillation and, with the component again oriented horizontal, initiate a +90 to -90 degree rocking rotation at a speed of about 14 rpm for about 150 seconds.
- d. Repeat step b.
- e. Repeat step c.
- f. Repeat step b.

## [Para 27] [0027] Ninety-degree integer rotation without oscillation:

- a. Initiate coating process by depositing for about 50 seconds while the component is held stationary in the horizontal position.
- b. Rotate the component about ninety degrees and hold for about 50 seconds.
- c. Continue periodic rotation and hold procedure at 50 second intervals.

## [Para 28] [0028] Constant rotation with integer oscillation:

- a. Initiate coating process by depositing for about 100 seconds while the component is substantially horizontal and is rotated at a substantially constant 14 rpm.
- b. Oscillate (pitch) the component down to about forty degrees from horizontal and hold for about 50 seconds while maintaining 14 rpm constant rotation.
- c. Oscillate (pitch) the component up to about forty degrees from horizontal and hold for about 50 seconds while maintaining 14 rpm constant rotation.
- d. Repeat step b.
- e. Repeat step c.

[Para 29] [0029] Constant rotation with stepped oscillation:

- a. Initiate coating process by depositing for about 100 seconds while the component is substantially horizontal and is rotated at a substantially constant 14 rpm.
- b. Oscillate (pitch) the component down to about forty degrees from horizontal and hold for about 50 seconds while maintaining 14 rpm constant rotation.
- c. Return the component to horizontal and hold for 50 seconds while maintaining 14 rpm constant rotation.
- d. Oscillate (pitch) the component up to about forty degrees from horizontal and hold for about 100 seconds while maintaining 14 rpm constant rotation.
- e. Repeat step b.
- f. Repeat step c.
- g. Repeat step d.

[Para 30] [0030] Constant rotation with oscillation to increase waviness of the TBC:

- a. Initiate coating process by depositing for about 120 seconds while the component is substantially horizontal and is rotated at a substantially constant 14 rpm.
- b. Oscillate (pitch) the component down to about forty degrees from horizontal over an extended interval of about 30 seconds while maintaining 14 rpm constant rotation.
- c. Hold the component in the forty-degree down orientation for about 100 seconds while maintaining 14 rpm constant rotation.
- d. Return the component to horizontal over an extended interval of about 30 seconds while maintaining 14 rpm constant rotation.
- e. Hold the component at the horizontal orientation for about 100 seconds while maintaining 14 rpm constant rotation.
- f. Oscillate (pitch) the component up to about forty degrees from horizontal over an extended interval of about 30 seconds while maintaining 14 rpm constant rotation.

- g. Hold the component in the forty-degree up orientation for about 100 seconds while maintaining 14 rpm constant rotation.
- h. Return the component to horizontal over an extended interval of about 30 seconds while maintaining 14 rpm constant rotation.
- I. Hold the component at the horizontal orientation for about 100 seconds while maintaining 14 rpm constant rotation.
- j. Repeat steps b-I.

[Para 31] [0031] In view of the above, modulated TBC microstructures can be obtained using existing processing technology with equipment operated in a modified manner to achieve the desired rotation, rocking and oscillation of a component. As a result of the improved impact resistance of the modulated microstructure that reduces the likelihood of TBC spallation at the TBC/bond coat interface, TBC's of this invention are believed to be capable of surviving on surfaces of components that are prone to impact spallation, including the leading edges of turbine blades and vanes.

Figure 4 is a microphotograph representative of an [Para 32] [0032] EBPVD-deposited columnar 7%YSZ TBC of the prior art (e.g., corresponding to Figure 1) and having a spalled region as a result of impact damage. For comparison, Figures 5 and 6 are microphotographs of two 7%YSZ TBC's deposited by EBPVD to a thickness of about 250 micrometers) with modulated microstructures in accordance with the present invention. The TBC of Figure 5 was deposited using the "on/off oscillation with constant rotation" procedure described above, and the TBC of Figure 6 was deposited using the "stepped oscillation with constant rotation" procedure described above. These TBC's underwent a standard particle impact test performed at about 2230°F (about 1220°C) using alumina particles with diameters of about 560 micrometers, fired in clusters of about 100 grams at about 30 feet per second (about 10 m/s). Using such a test, an average of about 105 grams of particles per mil (about 25 micrometers) of coating thickness would be sufficient to completely spall a region of a standard 7%YSZ TBC (e.g., Figure 4). In contrast, about 120

grams of particles per mil of coating thickness were required to completely spall a region of the TBC of Figure 5 (an improvement of about 14%), and about 145 grams of particles per mil of coating thickness were required to completely spall a region of the TBC of Figure 6 (an improvement of about 38%).

[Para 33] [0033] While the invention has been described in terms of particular embodiments, it is apparent that other forms could be adopted by one skilled in the art. Therefore, the scope of the invention is to be limited only by the following claims.

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